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Synthesis of a new bis(perfluoroalkyl oxirane) dioxyethylene ether

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Abstract

Classic direct synthetic methods failed to transform bis(perfluoroalkylallyl) dioxyethylene ether into the corresponding bis(perfluoroalkyl oxirane). This transformation was instead realized using a mixture of mercuric acetate/bromine to produce the corresponding bromoacetate, which was subsequently transformed to a bromohydrin and further to bis(perfluoroalkyl oxirane) through the use of triethylbenzyl ammonium chloride as a phase transfer catalyst in alkaline media.

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Keywords: Bis(perfluoroalkylallyl) ethers; Perfluoroalkyl oxirane; Dialkene ethers; Epoxidation; Dioxirane

1. Introduction

Highly fluorinated compounds have been described as useful in a wide range of applications. They are commonly used as surfactants [1], agrochemicals [2], industrial chemicals [3], HIV anti-viral drugs [4], medically useful materials (e.g., as blood substitutes) [5], pharmaceutical compounds [6] and biological agents [7]. Polyoxyethylene ethers are likewise known for their biological and medicinal uses [8,9] and especially for their biodegradable properties [10].

Oxirane compounds have been applied in a number of fields, including as pharmaceuticals [11], medicine [12], polymers [13], surfactants [14], and lubricants [15–17]. As these compounds are scientifically interesting, they have been used both as starting materials and as reaction intermediates in a number of different fields [18,19], such as polymer science [20], asymmetric synthesis [21], combinatorial chemistry [22], and microwave synthesis [23]. Their wide ranging importance across chemical sciences has cultivated a great interest in their syntheses [24] through routes using peracids [25], chlorate ions [26] halohydrins [27] or other catalytic methods [28]. Their structures [29,30] vary from simple [31] to asymmetric [32] or as complex systems [33].

The preparation of perfluoroalkyl oxiranes [34] from perfluoroalkene was first reported by Tarran et al. [35], after which a number of other methods appeared in the literature [36]. The lone direct epoxidation of perfluoroalkyl ethene was performed using a potentially hazardous mixture of H₂O, CH₃CN, and F₂ [37]. Indirect methods generally proceed through the initial synthesis of the corresponding bromoacetate using a mercuric

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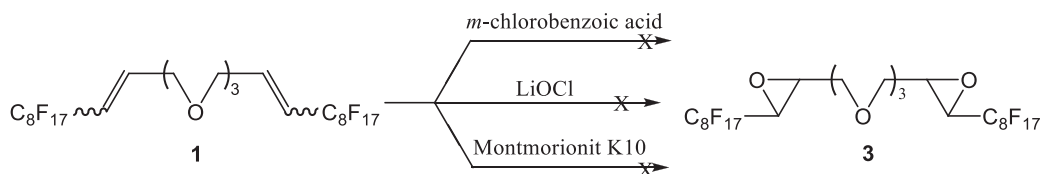
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Scheme 1. Failed direct epoxidation methods of bis(perfluoroalkyl allyl) **1**.

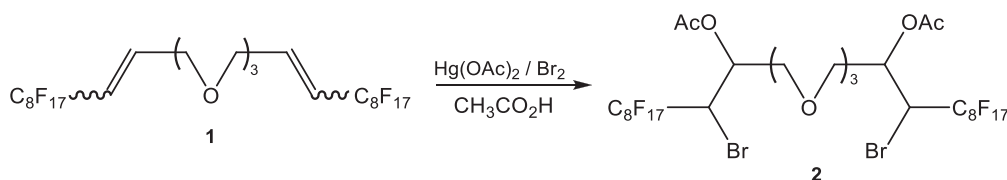
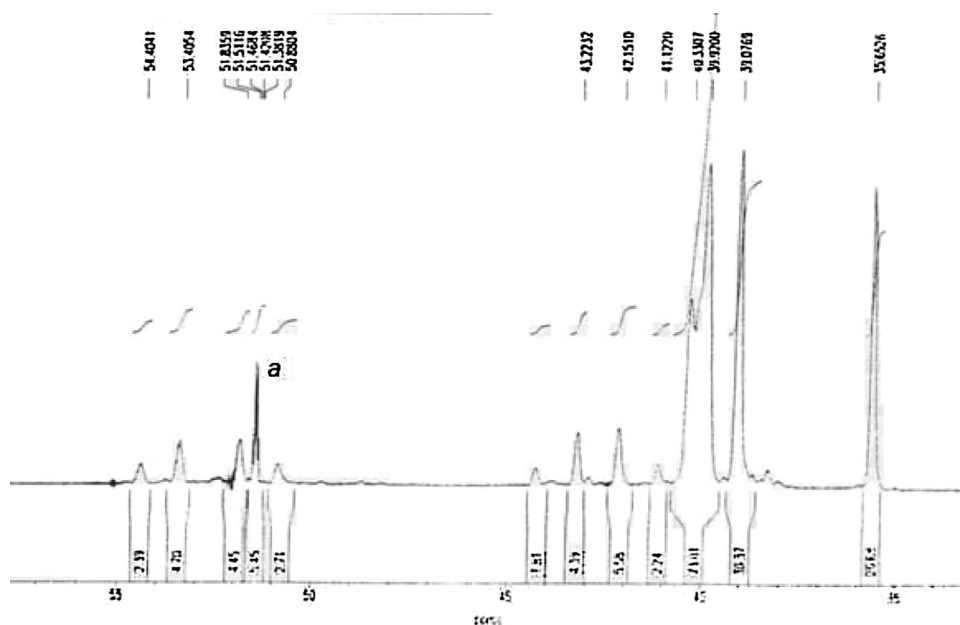
acetate/bromine mixture in acetic acid [36(g)]. Different methods have been described for the following steps [36], but the best results were obtained in our laboratory, as reported by Chaabouni et al., using 50% aqueous sodium hydroxide in the presence of a phase transfer catalyst (PTC). The optimal system consisted of triethylbenzyl ammonium chloride and a mixture of organic solvents, such as Et₂O/CH₂Cl₂ [38].

We have previously demonstrated the preparation of bis(perfluoroalkyl allyl) polyoxyethylene ethers [39]. As a continuation and in an attempt to synthesize the corresponding bis(perfluoroalkyl oxirane), we herein describe the synthesis of bis(heptafluoroalkyl oxirane) dioxethylene ether.

2. Results and discussion

Addition reactions to bis(perfluoroalkyl allyl) dioxethylene ether **1** are possible but require harsh conditions. For the synthesis of bis(perfluoroalkyl oxirane) **3**, we tested a number of direct epoxidation methods using *m*-chloroperbenzoic acid [40], lithium hypochlorite [41], and montmorionite K10 [42], but all of these methods failed to give the desired product (Scheme 1).

Therefore, we adopted an indirect method proceeding through the bromoacetate **2**, synthesized from bis(perfluoroalkyl allyl) dioxethylene **1** in conjunction with a mixture of mercuric acetate/bromine

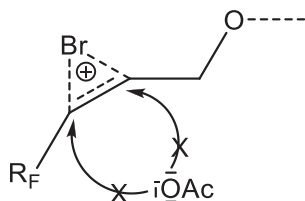
Scheme 2. Synthesis of (perfluoroalkyl bromoacetate) dioxethylene **2**.Scheme 3. ¹⁹F NMR spectrum of (perfluoroalkyl bromoacetate) dioxethylene **2**.

in acetic acid at room temperature (Scheme 2) [37]. The reaction was slow (15 days) and gave a low yield (35%), perhaps as a result of the low solubility of highly fluorinated **1** and its limited reactivity in addition reactions.

Starting from a mixture of *E/Z* isomers [39], only the *E* isomer of **1** was converted to the bromoacetate **2**. This synthetic step is non-stereoselective as the two faces of the ethylenic group are equivalent. The *EE* isomer of the bis(perfluoroalkyl allyl) dioxyethylene yielded the corresponding bromoacetate **2** as a mixture of diastereomers, which were identical by NMR.

In the ^{19}F NMR spectrum of bromoacetate **2**, the $\text{CF}_{2\alpha}$ fluorine atoms appear as an *AB* doublet centered at -120.2 ppm and -110.3 ppm with $^2J_{\text{FF}} = 281$ Hz (Scheme 3). The *Z* isomer was unreactive, as confirmed in the ^{19}F NMR spectrum of the crude product showing a signal at -111.5 ppm, corresponding to the $\text{CF}_{2\alpha}$ of the allylic isomer *Z* (signal a, Scheme 3). The ^1H NMR spectrum of the unreacted isomer displayed a signal for the allylic proton.

Even after formation of the bromonium ion intermediate, back-side attack by the AcO^- anion is nearly impossible due to the steric bulk of the perfluoroalkyl and dioxyethylene chains present on the same side of the double bond in the *Z* form (Scheme 4).



Scheme 4. Forbidden addition of Br/OAc on the *Z* form of bis(perfluoroalkyl allyl) dioxyethylene **1**.

Use of the method previously described by Chaabouni *et al.* [38] allowed us to prepare bis(perfluoroalkyl oxirane) dioxyethylene **3** (Scheme 5). Bromoacetate **2** was converted to the corresponding bromohydrin using a 50% aqueous sodium hydroxide solution and was then transformed *in situ* to bis(perfluoroalkyl oxirane) dioxyethylene ether **3** by the addition of a PTC (triethylbenzyl ammonium chloride) in an equal-volume

mixture of diethylic ether/dichloromethane. After stirring for 10 h, diepoxyde **3** was obtained in a 55% yield.

The new di(perfluoroalkyl oxirane) dioxyethylene ether **3** may have interesting physical and chemical properties as it bears two oxirane side groups, each capable of undergoing a large number of nucleophilic reactions.

Generalization of this reaction to other bis(perfluoroalkyl allyl) polyoxyethylenes **1** was not carried out due to the low yield of the first step, the long reaction time, and the lack of stereoselectivity in the synthesis of diepoxyde **3**.

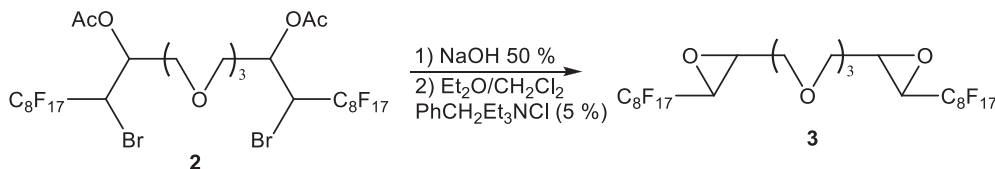
3. Conclusion

A new bis(heptadecafluoroalkyl oxirane) dioxyethylene was synthesized from the corresponding (perfluoroalkyl allyl) *via* a mixture of mercuric acetate/bromine followed by basic hydrolysis and cyclization in the presence of a PTC. Aside from the advantageous physical and chemical properties resulting from the perfluoroalkyl and polyoxyethylene chains, the presence of two oxirane groups on both sides provide the capacity for the di(perfluoroalkyl oxirane) dioxyethylene ether **3** to undergo a range of nucleophilic reactions. The syntheses of analogues of diepoxyde **3** from other perfluoroalkyl alkenes using different conditions are underway in our laboratory.

4. Experimental

4.1. Synthesis of bis(perfluoroalkyl bromoacetate) dioxyethylene **2**

A mixture of 4.5 mL of acetic acid, 1.8 g of mercuric acetate and 0.5 mL of bromine were added to a 25-mL round bottom flask equipped with a condenser at 0°C . Then, 3.5 mmol (3.58 g) of bis(3-perfluoroalkyl allyl) dioxyethylene **1** was slowly added. The mixture was stirred at room temperature for 15 days. At the end of the reaction, all solids were filtered and washed with water and ether. The filtrate was diluted in cooled water, washed with a solution of sodium thiosulfate, and decanted. The aqueous phase was extracted three times with ether after neutralization with a solution of



Scheme 5. Transformation of bis(perfluoroalkyl bromoacetate) **2** into the corresponding dioxirane **3**.

40% aqueous sodium hydroxide. The ether solutions were collected, neutralized with a carbonate potassium solution, and dried over sodium sulphate. After evaporation of the solvent, the residue was purified by column chromatography using a $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 70/30 eluent to obtain compound **2** as a viscous oil.

IR $\nu_{\text{C-F}} = 1000\text{--}1050\text{ cm}^{-1}$, $\nu_{\text{C-O-C}} = 1100\text{--}1120\text{ cm}^{-1}$ and $\nu_{\text{C=O}} = 1735\text{ cm}^{-1}$; ^1H NMR δ : 2.13 (s., 6H, 2 CH_3 -), 3.40–3.90 (m., 4H, 2 $\text{CH}_2\text{-O}$), 3.65–3.85 (m., 8H, 4 $\text{CH}_2\text{-O}$), 4.53 (m., 2H, 2CHBr), 4.96 (m., 2H, 2CH-O); ^{13}C NMR δ : 18.5 (s., 2C, 2 CH_3 -), 35.3 (m., 2C, 2CHBr), 69.1 (s., 2C, CH-O), 69.5 (s., 4C, 4 $\text{CH}_2\text{-O}$), 72.3 (s., 2C, $\text{CH}_2\text{-O}$), 105–120 (m., 16C, 16 CF_2 , 2 CF_3), 161.2 (s., 2C, 2C=O); ^{19}F NMR δ : –127.2 (m., 4F, 2 CF_2), –123.8 (m., 4F, 2 CF_2), –123.0 (m., 2 CF_2), –122.6 (m., 8F, 4 CF_2), –120.2 and –110.3 (AB syst. 4F, 2 $\text{CF}_{2\alpha}$, $^2J_{\text{FF}} = 281\text{ Hz}$), –82.0 (m., 6F, 2 CF_3 -, $^3J_{\text{FF}} = 10.97\text{ Hz}$) ppm.

4.2. Synthesis of bis(perfluoroalkyl oxirane) dioxethylene **3**

A solution of 2 g of sodium hydroxide in 2 mL of water was added to a two-neck 50-mL round bottom flask equipped with a condenser and a dropping funnel, which was placed on a magnetic stirrer prior to the addition of 0.8 mmol (1.04 g) of bis(perfluoroalkyl bromoacetate) dioxethylene **2** at 0 °C. The reaction mixture was stirred for 5 h at room temperature, followed by heating to 40 °C. Vigorous agitation was necessary due to the thickening of the solution. After 5 h of stirring at 40 °C, the mixture was cooled to 0 °C and 4 mL of an equal-volume mixture of $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ and 0.01 g of $\text{PhCH}_2\text{N}^+\text{Et}_3\text{Cl}^-$ (5%) were added. The mixture was stirred for 2 h at room temperature, filtered, washed, and extracted with ether ($3 \times 50\text{ mL}$). The solvent was evaporated and the residue was purified by column chromatography using a $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 80/20 eluent to obtain compound **3** as a viscous oil.

IR $\nu_{\text{C-F}} = 1000\text{--}1050\text{ cm}^{-1}$, $\nu_{\text{C-O-C}} = 1100\text{--}1120\text{ cm}^{-1}$; ^1H NMR δ : 3.45–3.60 (m., 6H, 2 CH_2 and 2CH), 3.65–3.76 (m., 8H, 4 $\text{CH}_2\text{-O}$), 3.92 (m., 2H, 2CH); ^{13}C NMR δ : 49.9 (m., 2C, CH- $\text{CF}_{2\alpha}$, $^3J_{\text{C-F}} = 27.52\text{ Hz}$), 58.5 (s., 2C, CH-O), 68.4 (s., 2C, CH_2O), 71.2 (s., 4C, CH_2O), 105–120 (m., 16C, CF); ^{19}F NMR δ : –123.0 (m., 4F, 2 $\text{CF}_{2\alpha}$), –123.9 (m., 4F, 2 $\text{CF}_{2\beta}$), –124.3 (m., 4F, 2 $\text{CF}_{2\delta}$), –124.9 (m., 4F, 2 $\text{CF}_{2\gamma}$), –127.3 (m., 4F, 2 $\text{CF}_{2\omega}$), –82.0 (6F, 2 CF_3 , $^3J_{\text{FF}} = 10.36\text{ Hz}$) ppm; HRMS calculated 1054.04548, found 1054.04498.

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